

Investigating the Band Gap and Flat Band Potential of Fe₂O₃ Doped with Ti, Ta, Sn and Zn

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Abstract

Investigating the Band Gap and Flat Band Potential of Fe₂O₃ Doped with Ta, Ti, Sn and Zn. Jeremiah Mann (University of California at Santa Cruz, Santa Cruz, CA 95001) John Turner (National Renewable Energy Laboratory, Golden, CO, 80401).

Iron oxide semiconductors are good choices for direct water splitting under solar illumination due to their band gap, stability in solution, ease of manufacture and material availability. Characterization of the semiconductor's properties is essential to pursue the goal of water splitting. Iron oxide semiconductors are doped with Ta, Ti, Sn and Zn of differing atomic concentrations ranging from 0.1% to 2% depending on material. The Fe₂O₃ samples are tested for band gap and flat band potential. The band gap, flat band potentials and dopant densities are determined.

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Introduction

Hydrogen used as an energy carrier is one of the most provocative prospects among several clean, sustainable, emerging energy systems. Direct water splitting by immersed semiconductors is the most direct means of producing hydrogen. For water splitting to occur, several characteristics of the semiconductor, such as band gap, flat band potential, overpotential and stability to corrosion must be optimized simultaneously (Aroutiounian et al., 2000; Beerman et al., 2000). Iron oxide semiconductors exhibit a band gap of ~ 2 eV, which is large enough to split water when illuminated with sunlight, but small enough to collect a significant fraction of solar radiation. Iron oxide is stable through a large pH range and, in general, oxide semiconductors are considered to be extremely stable materials. Added benefits are that the material is plentiful, cheap to manufacture and nontoxic. However, there are several drawbacks to iron oxide when it is used as a photoelectrode, such as low mobility of charge carriers due to a hopping mechanism of charge transfer (Sato, 1998; Beerman et al., 2000), and insufficiently negative flat band potential needed for spontaneous water splitting. The present work focuses on characterization of the samples and determining whether the different concentrations of dopants have changed the band gap or shifted the flat band potential to motivate further study of iron oxide semiconductors.

Materials and Methods

Semiconductor samples of iron oxide were prepared by doping Fe_2O_3 with the electroactive metal impurities. Several similar methods were used to create the ceramic semiconductors. They differed in sintering time, mixing medium, and concentration level. An example is the following process to make the $\text{Fe}_2\text{Ti}_{0.01}\text{O}_3$. Corresponding amounts of Fe_2O_3 and TiO_2 , were mixed individually at appropriate concentrations in distilled water, and after preliminary sintering in the air at 1100°C for 3 hours, the material was pressed into compact pellets. These pellets were then sintered in air at temperatures of 1200°C and 1300°C for 10 hours (Shakhnazaryan et al, 1993). Purity was tested with X-ray spectroscopy (Aroutiounian et al, 2000). Ohmic contacts were made by vacuum deposition of copper. Samples were 1 mm thick, and due to cutting specifics, varied in surface area. The samples were then mounted onto copper wire using conducting silver paint. The wire and semiconductor was then inserted into approximately 4 inches of glass tubing, and all surfaces on the sample end of the glass tube except for the semiconductor's front surface was covered with epoxy resin. Laboratory conditions for the investigation of the band gap were carried out using light generated from a tungsten lamp drawing 10 amps, a Stanford Research Systems SR530 lock-in amplifier, a Princeton Applied Research Verastat 2 potentiostat, a light chopper operating at ~ 24 Hz and a conventional cell with a platinum counter electrode with a saturated calomel reference electrode (SCE) in a buffer 7 solution (Mirovsky and Tenne, 1981; Tenne and Mirovsky, 1982).

The conditions for investigating the flat band potentials using Mott-Schottky analysis were carried out using the Solartron SI 1260 lock-in amplifier, SI 1287 potentiostat, and a

cell with platinum counter electrode, SCE reference electrode in a solution of 1 molar KOH in the dark. Data was collected at frequencies ranging between 10,000 Hz, 1000 Hz, 100 Hz, 50 Hz. (Gartner, 1959; Bockris and Khan, 1993, p. 486-489).

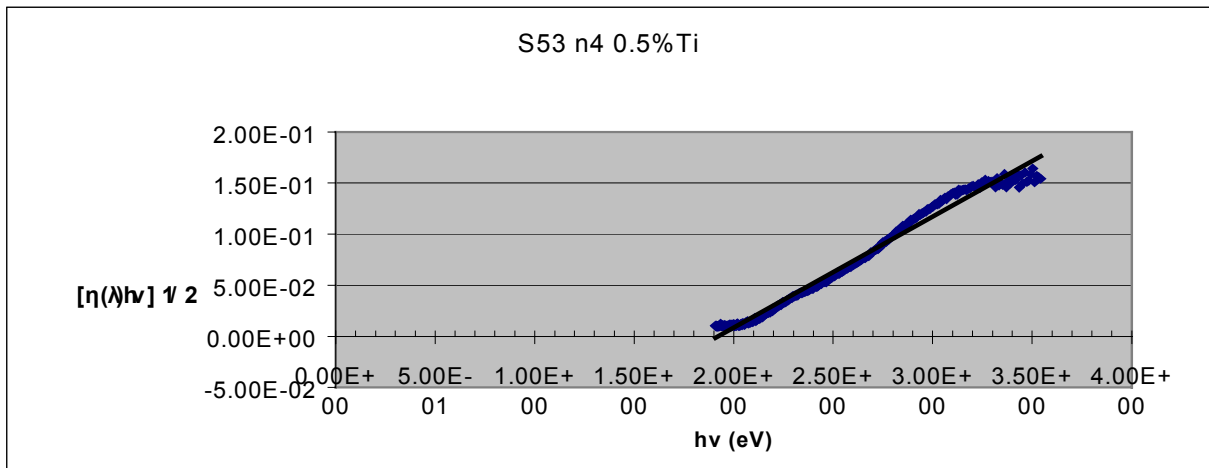
Results

The experimentation resulted in the characterization of 17 different Fe_2O_3 semiconductors. Band gaps of all the semiconductors were extrapolated using the following equation (Akikusa and Khan, 1997; Pankove, 1975 pg. 34-44)

$$\eta(\lambda)h\nu = A(h\nu - E_g)^n \quad (1)$$

Where A is a constant relating to the effective mass of the electrons and holes and n equals either 0.5 for allowed direct transitions, or 2, for allowed indirect transitions. (Pankove, 1975 pg. 34-44). Graph 1 shows the band gap of sample S53 n4 0.5% Ti obtained from the intercept of $[\eta(\lambda)h\nu]^{1/2}$ vs. $h\nu$ plot.

Graph 1.



Equation 1 is appropriate to use when the applied potential is much less than the flat band potential (Pankove, 1975 pg. 34-44). During this experiment the applied potential ranged between 0.1 v and 0.4 v, mainly remaining near 0.1 v. The flat band potentials ranged between -0.95 v and -1.90 v. The band gap (indirect) and the direct transitions agreed with published values for the material. Two samples: S56 n8 1.0% Ta and S56 n9 1.5% Ta, shifted the band gap down to 1.88 eV and 1.84 eV, respectively.

It is well known that the flat band potential (V_{fb}) of a semiconductor can be obtained from the intercept of the Mott-Schottky plot using equation 2 (Khan and Akikusa 1999; Bockris and Khan, 1993, pg. 489). C is the space charge capacitance, ϵ is the dielectric constant, ϵ_0 is the permittivity of a vacuum, N_d is the donor density, V_{app} is the applied potential, V_{fb} is the flat band potential and kT/e_0 is the temperature dependent term.

$$1/C^2 = (2/e_0\epsilon\epsilon_0N_d)[(V_{app}-V_{fb})-kT/e_0] \quad (2)$$

Graph 2 shows the V_{fb} for sample S53 n4 0.5% Ti obtained from the intercept of $1/C^2$ vs. applied potential as shown on the next page.

Graph 2.

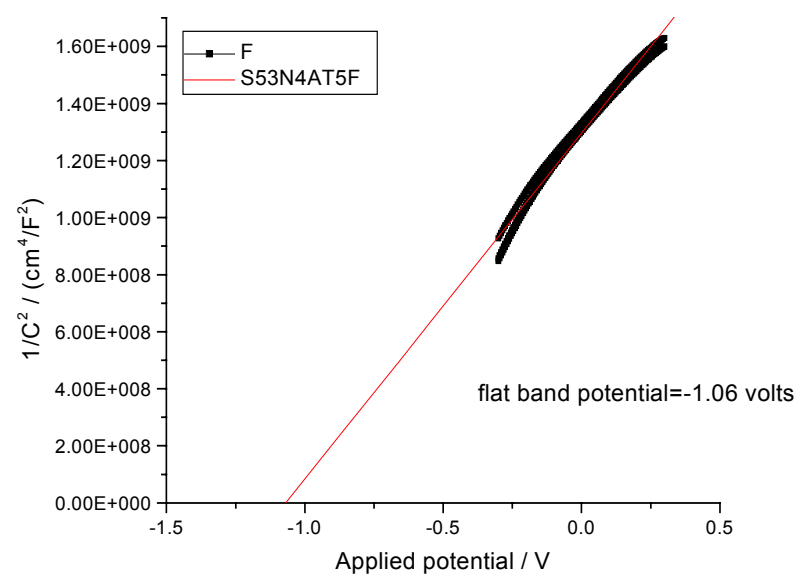


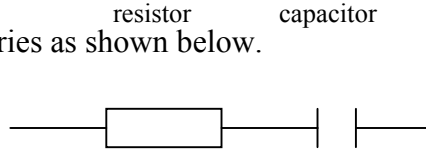
Table 1 Band gap and Flat Band Potentials for Fe₂O₃ samples

Fe ₂ O ₃ Samples	Band gap	Direct transition	Flat band potential at 50 Hz
S44 N3 1% Zn	1.93 (i)	2.7	*
S53 N1 0.1% Sn	1.98(i)	2.72	*
N3 0.1% Ti	2.06(i)	2.74	-1.46
N4 0.5% Ti	2.00(i)	2.22	-1.06
S56 N2 0.5% Sn	1.99(i)	2.71	-1.49
N3 1% Sn	1.98(i)	2.70	*
N4 1.5% Sn	1.96(i)	2.74	*
N5 1% Sn	1.99(i)	2.68	*
N5 2% Sn	1.98(i)	2.66	*
N7 0.5% Ta	1.92(i)	2.66	-0.95
N8 1% Ta	1.88(i)	2.62	-1.14
N9 1.5% Ta	1.84(i)	2.69	-1.26
N10 2% Ta	1.91(i)	2.67	-1.21
			(1000Hz)
			-1.26
			(100Hz)
			-1.53
			(50Hz)
S58 N5 1% Ti	1.98(i)	2.69	-1.90
N6 1.5% Ti	1.97(i)	2.67	*
N6 1.5 Ta	1.98(i)	2.71	*
N7 2% Ti	2.00(i)	2.68	-1.43
			* Asterisk means data gave no result using simple circuit model

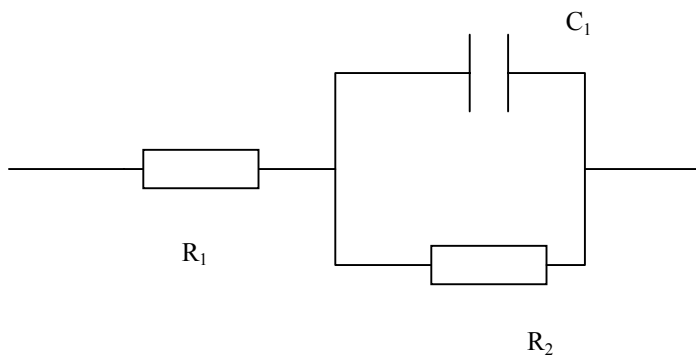
Discussion and Conclusions

Band gaps were calculated for all the Fe_2O_3 samples. Two of the samples showed a decrease in band gap. Further investigation is needed to determine if the dopants were responsible for the shift.

Mott-Shottky analysis was done using a simple circuit model composed of a resistor and capacitor in series as shown below.



The capacitor modeled the space charge layer created in the semiconductor (Aroutiounian et al, 2000; Aroutiounian et al, 1999). The results of the experiments indicated that the simple model is insufficient to account for the response of some of the samples. In fact for these samples, in a range of 10,000 Hz to 50 Hz they gave no reasonable data. The flat band potentials recorded varied over a range of -1.05 volts indicating that the simple circuit model is insufficient. Lastly, the dopant densities were calculated using the $(2/e_0\epsilon\epsilon_0N_d)$ term from equation 2. This term is equal to the slope of the line give by the $1/C^2$ vs. voltage plots. Therefore, the dopant density (N_d) is easily calculated. The magnitudes of the dopant densities ranged between 10^{21} and 10^{23} which is abnormally high. A possible explanation for this is the surface of the semiconductor is porous creating a larger surface area compared to the measured area. This confirms that the independent variable intercepts that equal the flat band potential are incorrect. More experimentation using impedance spectroscopy and a more sophisticated circuit model, such as the one shown (Aroutiounian et al, 1999)



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